EFFECTS OF MASS TRANSFER AND HYDROGEN PRESSURE ON THE FIXED-BED PYROLYSIS OF SUNFLOWER BAGASSE

E. Putun [1], O.M. Kockar [1], F. Gercel [1], E. Ekinci [2], J. Andresen [3]
M.M. Maroto-Valer [3] and C.E. Snape [3]

(1) Anadolu University, Dept. of Chemical Engineering, Faculty of Engineering & Architecture, 26470 Eskisehir, Turkey
(2) Istanbul Technical University, Dept. of Chemical Engineering, 80626 Istanbul, Turkey
(3) University of Strathclyde, Dept. of Pure & Applied Chemistry, Glasgow G1 1XL, UK

Keywords: Sunflower bagasse, pyrolysis, hydropyrolysis.

INTRODUCTION

There are a number of waste and biomass sources being considered as potential sources of fuels and chemical feedstocks [1]. The ecomomics for biomass pyrolysis are generally considered to be most favourable for (i) plants which grow abundantly and require little cultivation in arid lands and (ii) wastes available in relatively large quantities from agricultural plants, for example, sunflower and hazel nuts. For the former, one such group of plants is *Euphorbiaceae* which are characterised by their ability to produce a milky latex, an emulsion of about 30% w/w terpenoids in water. One species in the family, *Euphorbia Rigida* from Southwestern Anatolia, Turkey is cultivated in close proximity to the sunflower growing regions and their oil extraction plants. The Turkish sunflower oil industry generates 800,000 tons of extraction residue (bagasse) per annum. Thus, both sunflower wastes and latex-producing plants are being considered as feedstocks for a future thermochemical demonstration unit in Turkey. It was demonstrated previously [2] that much higher oil yields can be obtained from *Euphorbia Rigida* by static retorting than by the traditional method of low temperature solvent extraction (18 cf. 10% daf basis). However, it is well known from studies on coals and oil shales (see, for example, references 3 and 4) that oil yields are severely limited under static retorting conditions and, as a consequence, flash pyrolysis processes, particularly fluidised-beds, have received considerable attention for converting biomass to liquid products [5,6]. In contrast, pyrolysis at relatively high hydrogen pressures (hydropyrolysis) has not been widely investigated for biomass. A potential advantage of hydropyrolysis is the ability to upgrade tar vapours over hydroprocessing catalysts [7].

For *Euphorbia Rigida* , it was reported previously that an oil yield of *ca* 40% caould be attained by hydropyrolysis at 150 bar pressure in a well-swept fixed-bed reactor [8]. However, the main effect of raising the hydrogen pressure was to decrease the oxygen content of the resultant oil and, thus, on a carbon basis, increase the fraction converted to oil [9]. This study extends the previous investigation on *Euphorbia Rigida* to sunflower bagasse to ascertain the most appropriate pyrolysis regime for attaining oils in high yield with low oxygen contents.

Fixed-bed pyrolysis (atmospheric pressure) and hydropyrolysis experiments at temperatures in the range, 400-700°C have been conducted on sunflower bagasse to assess the effects of mass transfer and hydrogen pressure on oil yield and quality,. NMR characterisation of the liquid products and chars has been used to assess the extent of aromatisation of the cellulosic structure during pyrolysis.

EXPERIMENTAL

Pyrolysis experiments have been carried out on sunflower bagasse samples obtained from both pressing and solvent extraction. For the pressed sample, a number of particle sizes and gas sweep velocities were used in a Heinze retort (40 g sample) with a heating rate of 7°C min^{-1}. A faster heating rate of 300°C min^{-1}

was employed for atmospheric pressure pyrolysis experiments in a well-swept resistively-heated fixed-bed reactor (5 g sample) [10] which was also used for tests with hydrogen pressures of 50, 100 and 150 bar on all the samples investigated.

The product oils have been characterised by elemental and ^{1}H NMR analyses and column chromatographic separations. Solid state ^{13}C NMR analysis was conducted on the bagasse samples and a selection of the chars. Cross-polarisation-magic-angle spinning (CP-MAS) spectra were obtained using a Bruker MSL100 spectrometer with a contact time of 1 ms.

RESULTS AND DISCUSSION

Pyrolysis Figures 1 and 2 indicate that in the Heinze retort, overall conversions (100 - %char), oil and water yields are fairly independent of both particle size and the sweep gas flow rate for the pressed bagasse sample. As the flow rate is reduced from 600 to 100 cm^3, the oil yield decreases by no more than 5% from the maximum value of close to 40% (daf basis). Similarly, the smallest (0.4 mm) and largest (>1.8 mm) particle sizes used give only *ca* 3% less oil than the intermediate sizes (Figure 2). Indeed, the overall conversions of nearly 80% achieved in the Heinze retort are the same as those in the resistively-heated fixed-bed reactor (Figure 3) where the gas velocity is an order of magnitude greater. The conversions are somewhat lower for the extracted bagasse than for the

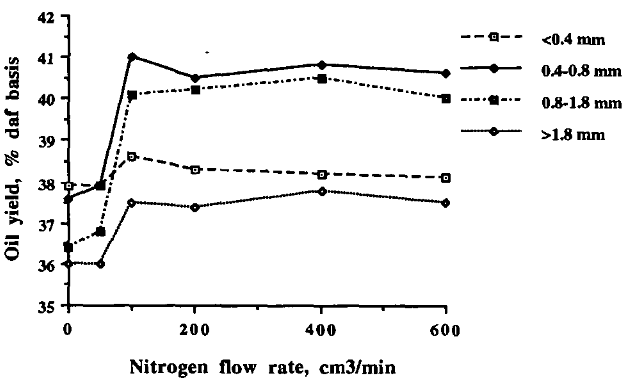

FIGURE 1 EFFECT OF PARTICLE SIZE AND GAS FLOW RATE ON OIL YIELDS IN HEINZE RETORT

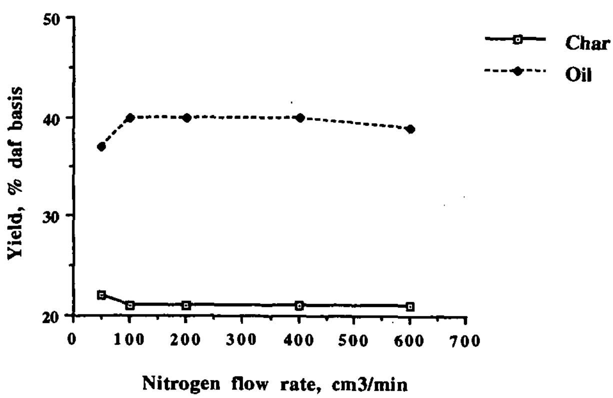

FIGURE 2 EFFECT OF GAS FLOW RATE ON PRODUCT YIELDS IN HEINZE RETORT, 0.8-1.8 mm

pressed sample which contains more residual oil. These results suggest that mass transfer restrictions to volatile evolution are much less marked for the sunflower bagasse compared to coals and oil shales where oil yields are generally reduced significantly by decreases in carrier gas flow rate [3,4], as well as increases in particle size. This major difference is probably attributable to the low bulk density of the bagasse. A rotary kiln would thus suffice to ensure that the maximum oil yields are obtained on a pilot plant scale.

Hydropyrolysis Figure 4 compares the oil yields from the extracted bagasse sample with those obtained from *Euphorbia Rigida* and pure cellulose. Compared to coals and oil shales, the effects of hydrogen pressure on oil yield are seemingly much less pronounced. For the cellulose and *Euphorbia Rigida*, hydrogen pressure hardly affects oil yield which attains a broad maximum between 30 and 40% as the hydrogen pressure is increased from 50 to 150 bar at 520°C (Figure 4). The variation is somewhat more pronounced for the sunflower bagasse sample where the oil yield reaches a maximum at *ca* 100 bar and then decreases due to water formation (Figure 4). However, in all cases, hydrocarbon gas yields increase monotomically and char yields decrease with temperature. For example. the methane yield increased from 1.2 to 4.8% (daf basis) at 150 bar pressure for the extracted bagasse.

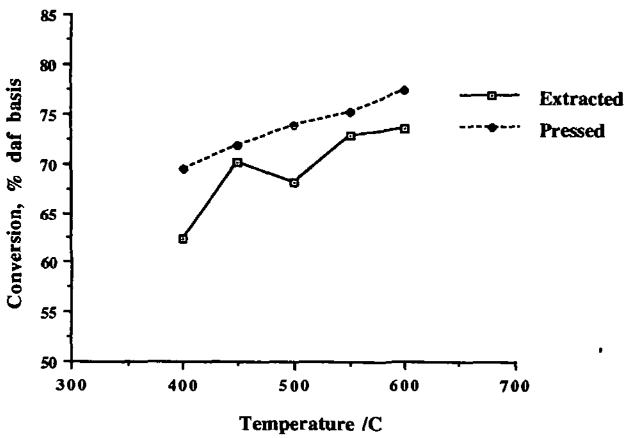

FIGURE 3 EFFECT OF TEMPERATURE ON CONVERSIONS IN FIXED-BED REACTOR

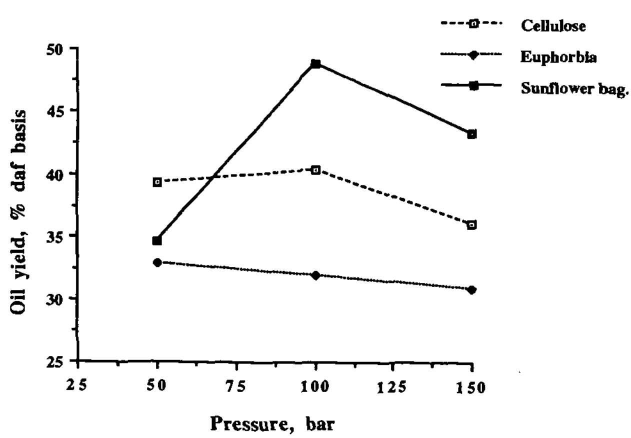

FIGURE 4 EFFECT OF HYDROGEN PRESSURE ON CONVERSIONS IN FIXED-BED REACTOR

Compositional information Table 1 compares the elemental compositions of the pressed bagasse with and an oil obtained from the Heinze retort. The product oil is characterised by a high oxygen content with a somewhat lower H/C ratio than the original bagasse. The typical ^{1}H NMR spectrum shown in Figure 5 indicates that a significant amount of the aliphatic carbon is still bound to oxygen (peaks in 3.5-5.5 ppm chemical shift range). The fact that most of the aromatic hydrogen intensity occurs in the 6.5-7.0 ppm range indicates that the aromatic species are largely phenolic. In addition to phenols, IR spectroscopy has indicated that carboxylic acids and ketones/aldehydes are also major oxygenates present in the polar fractions from open-column silica gel chromatography. The n-hexane and toluene eluates corresponding to alkanes and neutral aromatics, respectively accounted for 14 and 21% of the n-pentane-solubles. The alkanes and long alkyl moieties which give rise to the characteristic peak at 1.25 ppm in the ^{1}H NMR spectrum (Figure 5) are probably largely derived from lipids and residual oil in the bagasse. The relatively high nitrogen contents of the sunflower waste-derived oils (Table 1) present the major obstacle to producing hydrocarbon liquid products in two-stage hydropyrolysis where the tar vapours are passed over a hydroprocessing catalyst.

Figure 6 shows the CP/MAS ^{13}C NMR spectra of the pressed bagasse sample and the pyrolysis and 150 bar hydropyrolysis chars obtained at 500°C in the fixed-bed reactor. The bagasse still contains an appreciable concentration of lipid material (15-45 ppm) which is the precursor of the alkanes formed during pyrolysis. The lignin aromatic carbons in bagasse account for ca 10 mole%. Both the chars are highly aromatic in character with aromaticities of *ca* 0.95. However, small peaks at 70 and 180 ppm are evident in the pyrolysis char from residual ether/hydroxyl and carboxyl moieties. From the typical carbon aromaticities of 0.30 and 0.95 for the product oil and char and their respective yields of *ca* 25 and 35% (Figures 1-3), it is estimated that 40% of the initial carbon has aromatised during pyrolysis at 500°C.

Table 1 Elemental compositions of pressed bagasse, Heinze retort oil and char

		Bagasse (daf basis)	Oil	Char
	C	49.6	69.4	77.9
%	H	7.4	9.5	2.6
	N	4.4	5.1	5.1
	O (by difference)	38.5	16.0	14.4
	Atomic H/C	1.78	1.63	0.40

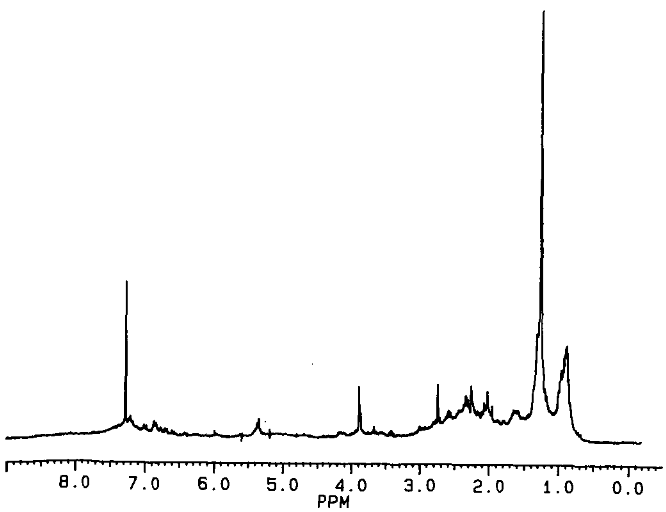

FIGURE 5 ^{1}H NMR SPECTRUM OF HEINZE RETORT OIL

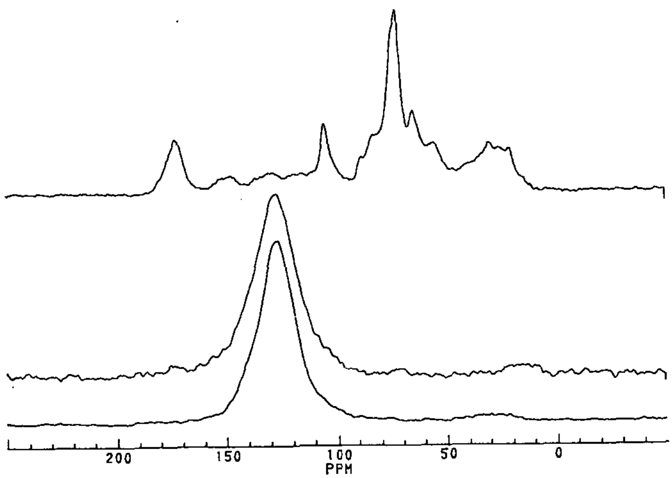

FIGURE 6 ^{13}C NMR SPECTRA OF PRESSED BAGASSE (top), A NITROGEN CHAR (middle) AND A HYDROPYROLYSIS CHAR (bottom)

CONCLUSIONS

In contrast to coals and oil shales, oil yields from the sunflower bagasse were found to be largely independent of particle size (<2 mm) and sweep gas velocity with *ca* 40% w/w oil (dry basis) being obtained at 450-500°C in both the Heinze retort and fixed-bed reactor. The use of high hydrogen pressures (> 50 bar) increased the oil yields by up to *ca* 10% w/w but these increases are much greater when expressed on a carbon basis due to the reduced oxygen contents of the oils. Even at low pressure, it has been estimated that *ca* 40% of the initial carbon aromatised during pyrolysis.

ACKNOWLEDGEMENTS

The authors thank the Science & Engineering Research Council and the Deaprtment of Trade & Industry for financial support (Grant no. GR/J/08997). FG thanks British Gas for a University of Strathclyde Scholarship.

REFERENCES

1. Sofer, S.S. and Zaborsky, O.R, Biomass energy conversion processes for energy and fuels, Elsevier Applied Science, London (1981).
2. E. Putun, S. Besler, A.E. Putun and E. Ekinci, Chimica Acta Turcica, **17**, 307(1989).
3. C. Bolton, C.E. Snape, R.J. O'Brien and R. Kandiyoti, Fuel, **66**, 1413 (1987).
4.. E. Ekinci, A.E. Putun, M. Citiroglu, G.D. Love and C.J. Lafferty and C.E. Snape, Fuel, **71**,1192 (1992).
5. N.Y. Chen, D.E. Walsh and L.R. Koenig, Ch24, p 279 in Pyrolysis Oils from Biomass, Producing, Analysing and Upgrading, ACS 376 (1988).
6. D. Scott and J. Piskorz, Can. J. Chem. Eng., **60(5)**, 664 (1982).
7. H.P. Stephens, C. Bolton and C. E. Snape, Fuel, **68**, 161 (1989).
8. E. Putun, C.J. Lafferty, F.J. Donald, C.E. Snape and E. Ekinci in Proc. Int. Conf. on Advances in Thermochemical Biomass Conversion, Ed. A.V. Bridgewater (1993).
9. F. Gercel, M. Citiroglu, C.E. Snape, E. Putun and E. Ekinci, Fuel Process. Technol., **36**, 299 (1993).
10. C.E. Snape, C.E. and C.J. Lafferty, Prepr. Am. Chem. Soc. Div. Fuel Chem., **35**, 1 (1991).